

Development of an *In-Situ* Mass Spectrometer for Stable Isotope Analysis

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LONG-TERM GOALS

Long-term goals for this project are to extend the use and application of small portable in-situ isotope ratio mass spectrometers for studies of a wide range of dissolved chemical species, including various forms of dissolved inorganic and organic carbon. Isotopic assessment of dissolved species can lead to the development of predictive tools for determining the biological-physical response of coastal oceans to natural climatic and anthropogenic changes, and to the seasonal development of physical boundary conditions (e.g., particle density distributions and perturbations in light transmittance).

OBJECTIVES

A miniature magnetic sector mass spectrometer from Intelligent Ion Inc. (Seattle, WA), equipped with a 100-Faraday cup array detector, was to be delivered to the Center for Ocean Technology (COT) at the University of South Florida (USF). After delivery, the mass spectrometer was to be integrated with a membrane introduction interface and tested for analysis of low-molecular weight gases (e.g., N₂, O₂, and CO₂) in air and water samples. System performance (precision and accuracy) of ¹³C/¹²C measurements for dissolved and gas-phase CO₂ was to be evaluated using gas standards, isotopically calibrated CO₂ reference gases and acidified reference sea water samples. Coulometric measurements of dissolved inorganic carbon (DIC) were also to be obtained for comparison with the mini-sector mass analyzer results. Using this approach we should be able to accurately determine not only instrument precision and accuracy, but also sensitivity and linearity, thereby constraining the range of possible applications. Ultimately the mass spectrometer is to be integrated into an underwater system for in-situ analysis.

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APPROACH

High precision measurements of stable isotope ratios are almost exclusively performed in the laboratory on large magnetic sector mass spectrometers. The most precise measurements of this type are made using sector mass spectrometers that simultaneously detect isotopes of interest.

Simultaneous detection using a sector mass spectrometer is the superior method for precise isotope measurements for a number of reasons: 1) the electronics required for this type of mass analyzer are simple, allowing a high degree of stabilization; 2) the duty cycle for each isotopic species is increased to essentially 100%; and 3) any fluctuations in instrumental parameters affect all mass intensity measurements, thereby nullifying effects on mass ratios. The highest absolute accuracy isotope ratio measurements are obtained using instruments of this type that also allow periodic comparison of measured sample ratios with standards of known isotopic composition.

No commercially available *portable* sector mass spectrometers for simultaneous isotopic monitoring has been available until Intelligent Ion, Inc. (Seattle, WA) very recently produced a miniature magnetic sector mass spectrometer^{1,2} with this facility. Their mass spectrometer, based on the Mattauch-Herzog design^{3,4}, is ideal for simultaneous detection, as it provides a linear double focus (angle and energy) over a very large mass range. The Intelligent Ion, Inc. design effects double focusing by placing a series of individual microfabricated Faraday cup detectors along the linear focal plane^{5,6}. For our application, we propose a design that will allow monitoring of at least 16 individual masses, so that *each molecular weight of interest will have its own detector element*. In addition, Intelligent Ion, Inc. has developed highly sensitive and rapid readout electronics coupled with each microfabricated detector element, resulting in satisfactory detection limits and a nearly 100% duty cycle for all monitored masses.

WORK COMPLETED

The Intelligent Ion, Inc. mass spectrometer was delivered in the late fall of 2002. Subsequent testing (which eventually involved a trip to USF by two Intelligent Ion, Inc. personnel), using both a membrane interface and a short gas chromatograph (GC) column interface, revealed that the sensitivity and detection limits of the system were below those required for the targeted measurements for this project. The two primary problems were high noise levels in the detection electronics, and the lack of a way to vary the detection integration time for different mass ranges. The result of the latter problem was that high intensity mass peaks (such as H₂O and N₂) would swamp the detection electronics before sufficient measurement times were achieved for the lower intensity mass peaks (such as CO₂). The instrument was subsequently returned to Intelligent Ion, Inc. for modification to address these problems.

The Intelligent Ion, Inc. system is scheduled to be returned to USF in October 2003 with the following upgrades. The mass spectrometer (MS) core was completely redesigned using Solidworks[®] to enable manufacturing by a supplier known for its high quality work (Scientific Instrument Services, Inc.) A photograph of the newly designed MS core is shown in Figure 1. Also, the previous 100-cup detector array will be replaced by a 200-cup array providing a 2x improvement in mass resolution. Variable integration periods will be included to boost the sensitivity of low intensity masses, and extensive work has been devoted to reducing noise in the detection electronics. In addition, the PC-104 central processor will be replaced by a Motorola Coldfire[™] processor for reduced power consumption and higher speed.

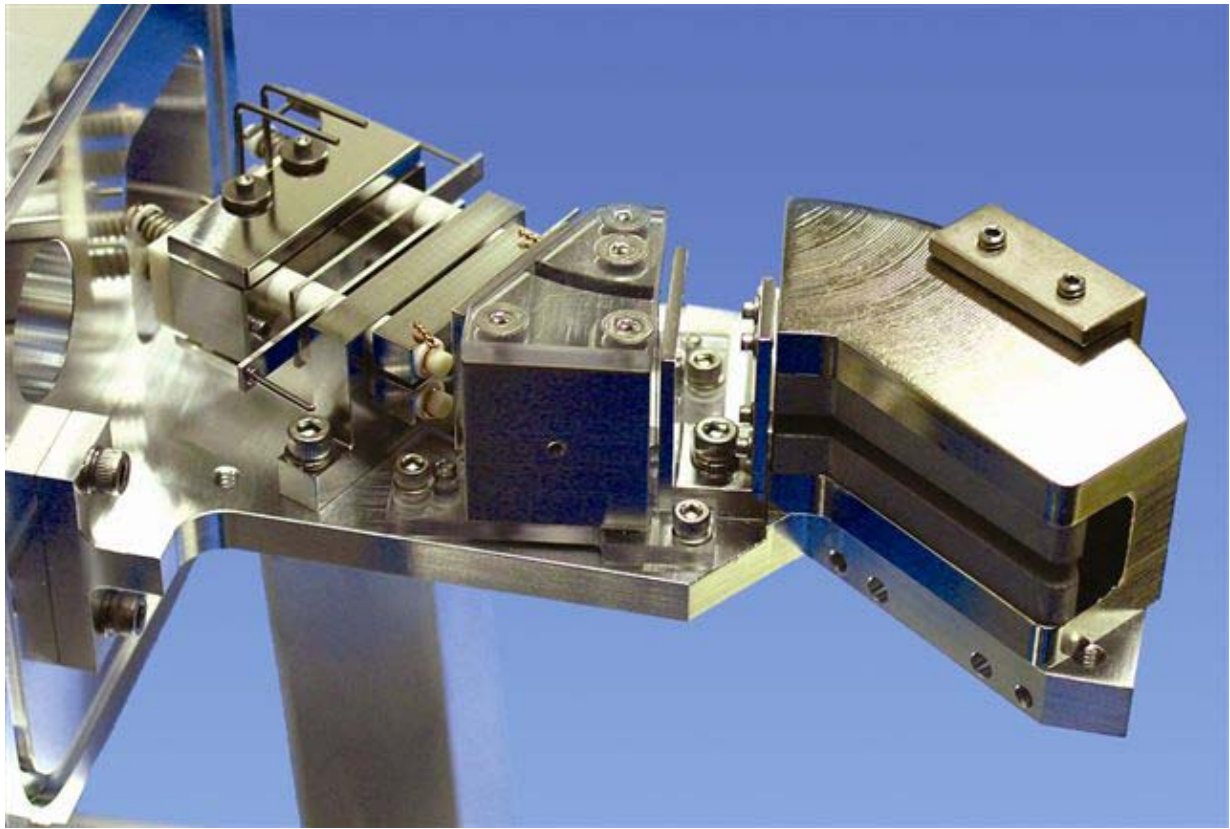


Figure 1. Intelligent Ion, Inc. new mass spectrometer core

In addition to the improvements made to the mass spectrometer system by Intelligent Ion, Inc., progress has been made at USF in other areas of the proposal as well. A majority of the components for the automated in-line acidification of seawater samples have been ordered, received and partially assembled. The gas bench acidification module, to be used for calibration of isotope ratios on a laboratory isotope ratio MS, has been ordered. All calibration gases and additional calibration equipment have been ordered and received.

RESULTS

Figures 2 and 3 show a recent mass spectrum of air obtained using the Intelligent Ion, Inc. mass spectrometer (to be returned to USF in October 2003). Table 1 shows quantitative data obtained from this spectrum regarding the signal-to-noise ratios for selected mass peaks. For acidified seawater samples, which have a CO₂ content much greater than air, the CO₂ signal-to-noise ratio is likely to surpass that of N₂.

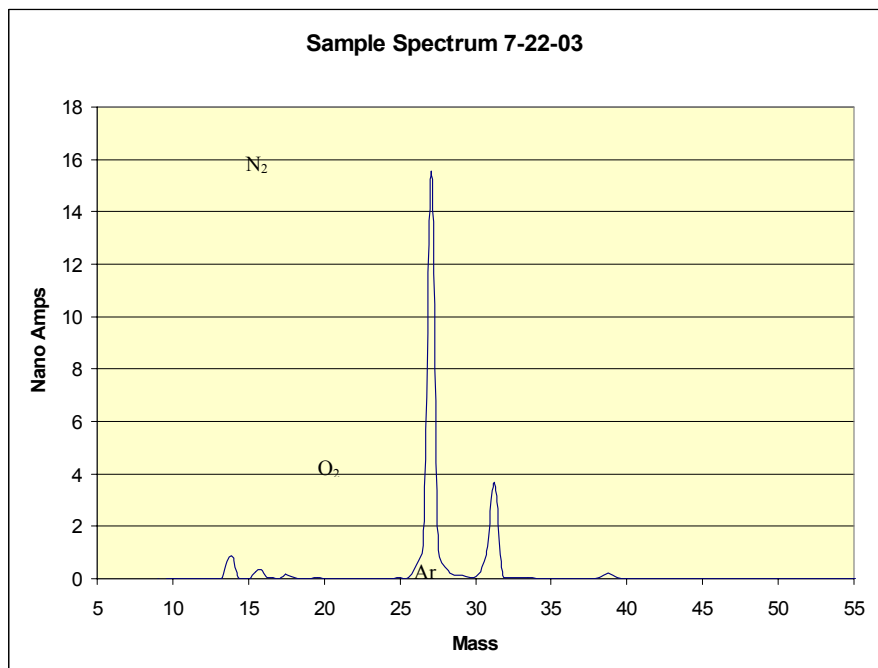


Figure 2. Mass Spectrum of Air

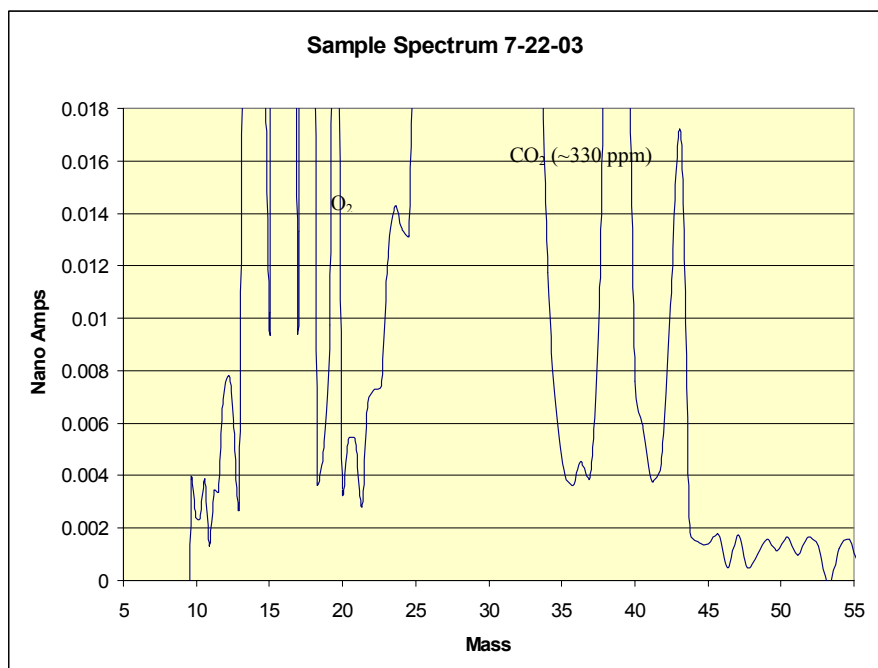


Figure 3. Same spectrum as Figure 2, 1000x zoom

Table 1. Signal-to-noise ratios

Signal to Noise Comparison (V)		Signal : Noise
N2	7.77359	9039.1 : 1
O2	1.83679	2135.8 : 1
Ar	0.11832	137.6 : 1
CO2	0.00851	9.9 : 1
Noise*	0.00086	

IMPACT/APPLICATIONS

The ability to perform in-situ isotopic analyses should have a profound impact on data acquisition rates. Rapid in-situ isotopic analysis should significantly advance capabilities to measure and model rapidly varying dynamic biogeochemical processes in the oceans and atmosphere. In addition to oceanic applications, a small portable mass spectrometer of this construction, with a 100% duty cycle and a broad mass range, should have broad high-value applications for both scientific and regulatory purposes.

RELATED PROJECTS

This project was a direct spin off from another ONR funded proposal “Development and Deployment of In-Situ Mass Spectrometers” Grant Number: N00014-98-1-0154.

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